

MULTI-LAYER DRY PAINT DECORATIVE LAMINATE HAVING
DISCOLORATION PREVENTION BARRIER

5 CROSS-REFERENCE TO RELATED APPLICATIONS

This is a continuation-in-part of U.S. Application No. 457,826, filed June 9, 2003, which is a continuation-in-part of U.S. Application No. 367,611, filed February 14, 2003. 10 These applications are incorporated herein in their entirety by this reference.

FIELD OF THE INVENTION

This invention relates generally to dry paint transfer 15 laminates, and more particularly, to a multi-layer dry paint decorative laminate having a barrier layer that inhibits migration of discoloration-causing pigments into color-producing layers of the laminate.

20 BACKGROUND

Dry paint transfer laminates have been used in the past as surface coverings that provide an alternative to conventional painting. Water based paints and oil based paints have well known shortcomings that can be overcome by 25 the use of decorative dry paint transfer films as a paint replacement. Environmental problems such as solvent evaporation from paint systems applied by spray painting also are avoided by use of decorative dry paint transfer films.

Such decorative dry paint transfer films are typically 30 applied to a substrate surface by an adhesive layer carried by the film. Use of heat-activated adhesives or water-activated adhesives can have certain disadvantages that are overcome by use of pressure-sensitive adhesives, by which the decorative film is adhered to the substrate surface by application of 35

pressure only, typically at room temperature. Examples of decorative films having pressure-sensitive adhesive layers for interior or exterior applications are disclosed in U.S. Patents 6,096,396 to Patton et al., 6,086,995 to Smith, and 5,229,207 to Paquette et al.

Decorative films having a pressure-sensitive adhesives are often adapted to facilitate application to a surface by using various forms of repositionable adhesives known in the art. The laminate can be initially applied to a surface, removed temporarily, and then repositioned, to allow the adhesive to form a permanent bond. Decorative films having such a repositionable adhesive layer are described, for example, in the '207 patent to Paquette et al.

The present invention comprises a multi-layer laminate adapted to be placed in contact with a surface which can be a painted surface. In films overlaying painted surfaces containing pigmented materials such as dyes or mono azo pigments, the colored materials may migrate or bleed into the overlaying film. This causes the finish to discolor. Pigments used in wall paints containing yellow pigments as a component, or to a lesser extent, orange or red pigments or dyes, can contain such mono azo constituents that can migrate from the wall surface through the overlaid film and into the color layer of the film, causing it to discolor.

The present invention provides a multi-layer laminate adapted for contact with a painted substrate surface containing organic materials with color constituents that will bleed or migrate; and the invention addresses a situation, in particular, where the painted surface containing the migrating organic color components may not be modified to avoid the color migration problem. In response to this problem, the invention provides a laminate containing one or more barrier

layers that cooperate to block or capture the migrating color materials, and in particular, those containing mono azo pigments. The barrier layer inhibits discoloration of the colored layer or layers in the laminate caused by the laminate contacting such a painted surface.

SUMMARY OF THE INVENTION

Briefly, the invention comprises a multi-layer laminate adapted to provide a layer of color to a painted surface. The laminate includes a pressure-sensitive adhesive for overlaying and contacting the painted surface. The laminate includes one or more barrier layers that slow or stop the migration of discoloration-causing pigments from the surface, through the adhesive layer, to the color layer of the laminate.

In one embodiment, the barrier will slow or stop the color change caused by mono azo pigments in interior latex paint. By applying a barrier layer of specific polymers and/or by addition of specific additive materials to the barrier layer, the color migration may be stopped or significantly reduced.

One embodiment of the invention comprises a decorative dry paint transfer laminate having a layer of dry paint, a pressure-sensitive adhesive layer on one side of the dry paint layer, and a release liner in releasable contact with the dry paint layer on a side opposite from the pressure-sensitive adhesive. The dry paint layer comprises a binder and a pigment. A barrier layer is positioned between the dry paint layer and the pressure-sensitive adhesive layer. The release liner is removable from the dry paint layer at room temperature. The pressure-sensitive adhesive is adapted for adhering the laminate to a substrate surface at room temperature. The substrate surface can be a painted wall

surface containing organic materials with color that can bleed or migrate. The pressure-sensitive adhesive layer adheres the laminate to the substrate surface under application of pressure. The release liner is then peeled away from the dry paint layer. The barrier layer comprises a thin, flexible film made from a material that stops or appreciably reduces migration of discoloration-causing constituents migrating from the painted surface through the adhesive layer to the color layer. In one embodiment, the barrier layer can comprise a polymeric material having a cross-linking density sufficient to inhibit transmission of discoloration-causing pigments and/or a dispersed additive that may capture or retard the migration of discoloration-causing pigments. The barrier layer is particularly useful in retarding or inhibiting the transmission of azo-type pigments and is present at a low coat weight or thickness which does not significantly increase the overall thickness of a decorative film. In one embodiment, the barrier thickness is no more than about 10% of the total thickness of the decorative film (excluding the outer releasable carrier film).

These and other aspects of the invention will be more fully understood by referring to the following detailed description and the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic cross-sectional view illustrating one embodiment of a multi-layer dry paint transfer laminate according to principles of this invention.

FIG. 2 is a schematic illustration of the dry paint transfer laminate self-wound into a roll form.

FIG. 3 is a schematic cross-sectional view showing an alternative embodiment of a dry paint layer contained in the laminate.

FIG. 4 is a schematic cross-sectional view showing another alternative embodiment of the dry paint layer.

FIG. 5 is a schematic cross-sectional view illustrating an alternative embodiment of the dry paint layer of FIG. 4.

FIG. 6 is a schematic cross-sectional view illustrating an embodiment containing a support layer.

FIG. 7 is a schematic cross-sectional view illustrating an embodiment containing a barrier layer.

FIG. 8 is a schematic illustration of a process for co-extruding a support layer and an adhesive layer used in one embodiment of the invention.

FIG. 9 is a schematic illustration of a process for co-extruding a support layer and an adhesive layer used in another embodiment of the invention.

FIG. 10 is a schematic view illustrating one embodiment of the invention which includes a dry paint layer, a barrier layer and a tie coat for the adhesive layer.

DETAILED DESCRIPTION

Referring to FIG. 1, a multilayer dry paint transfer laminate 20 is adapted for use as a surfacing film. The multilayer laminate includes a pigmented dry paint layer 22 comprising a synthetic resinous binder containing a dispersed pigment. The dry pigmented paint layer 22, also referred to herein as a color layer, generally can be a monocoat pigmented layer as illustrated in FIG. 1, or it can be combined with additional pigmented paint layers, coatings or print coats described below. In each instance, these decorative elements of the multilayer dry paint transfer film will be referred to generally as a decorative dry paint layer. In the illustrated FIG. 1 embodiment, the dry paint layer 22 has an upper surface 24 and a lower surface 26. The multilayer laminate further includes a dry adhesive layer 28 overlying and adhered to the upper surface 24 of the dry paint layer, and a flexible and foldable release liner 30 overlying and releasably adhered to the lower surface of the dry paint layer. The release liner has a matte release coat 32 on its inner surface for releasably adhering the release liner 30 to the lower surface 26 of the dry paint layer 22. The release liner 30 is adapted to be peeled away from the dry paint layer under an applied release force, also referred to herein as a carrier release function. The matte release coat 32 separates from the dry paint layer 22 but remains adhered to the release liner 30 when the release liner is peeled away from the dry paint layer. The release liner 30 also has an adhesive release coat layer 34 on a surface opposite from the dry paint layer. An exposed outer surface 38 of the adhesive release coat layer 34 is adapted for releasably contacting an exposed outer surface 40 of the adhesive layer 28 when the laminate is wound in a roll form illustrated in FIG. 2.

Referring to FIG. 2, the dry paint transfer laminate 20 is self-wound into a roll form with the outer exposed surface 38 of the adhesive release coat layer 34 in releasable contact with the exposed outer surface 40 of the adhesive layer 28. Thus, when the dry paint transfer laminate 20 illustrated in FIG. 2 is unwound, the adhesive release coat layer 34 on the release liner separates from the outer surface 40 of the adhesive layer 28 and remains adhered to the release liner 30. The matte release coat 32 remains adhered to the dry paint layer.

FIG. 3 illustrates a dry paint transfer laminate 42 which is identical to the dry paint transfer laminate 20 illustrated in FIG. 1, except that the decorative dry paint layer includes an optically transparent synthetic resinous clear coat layer 44 adhered to the lower surface 26 of the pigmented dry paint layer 22. In this embodiment, the outer clear coat layer 44 is in releasable contact with the matte release coat 32 of the release liner 30. When the release liner 30 is peeled away from the clear coat layer 44, the matte release coat 32 separates from the clear coat layer 44 and remains adhered to the release liner 30.

FIG. 4 illustrates a multilayer dry paint transfer laminate 46 which is identical to the dry paint transfer laminate 42 illustrated at FIG. 3, except that the decorative dry paint layer further includes a decorative print coat layer 48 between the pigmented dry paint layer 22 and the clear coat layer 44. The decorative print coat layer provides a decorative print pattern, and the pigmented dry paint layer 22 provides a background color and opacity for the decorative dry paint layer. The print pattern and background color are visible through the outer clear coat layer 44.

FIG. 5 illustrates a multilayer dry paint transfer laminate 50 which is identical to the dry paint transfer laminate 46 illustrated in FIG. 4, except that a second decorative print coat layer 52 can be printed or coated between the print coat layer 48 and the outer clear coat layer 44.

Additional print coat layers may be used. For instance, the multilayer laminate may contain up to about five or more print coats, and in one embodiment, preferably three or four print coat layers are used. The layers may have a print or design pattern using conventional printing methods, such as gravure, flexography, silk screen, or ink jet printing.

FIG. 6 illustrates an embodiment of a multilayer dry paint transfer laminate 54 which is identical to the multilayer laminate 20 illustrated in FIG. 1, except that the laminate 54 includes a flexible reinforcing layer 56 (also referred to herein as a support layer) between the dry paint layer 22 and the adhesive layer 28. The reinforcing layer 56 provides a means of structural support for the decorative dry paint layer and can provide additional opacity for the decorative dry paint layer. The reinforcing layer has a tensile strength which exceeds that of the dry paint layer or layers.

FIG. 7 illustrates another embodiment of the dry paint transfer laminate 58 which is identical to the laminate 20 illustrated in FIG. 1, except that the laminate 58 includes a flexible barrier layer 60 between the pigmented dry paint layer 22 and the adhesive layer 28. The intervening barrier layer can be used to inhibit or prevent undesired migration of constituents between the adhesive layer and the paint coat layer. Such barrier properties can include reducing or avoiding undesired discoloration by inhibiting or preventing

migration of pigments from an underlying substrate surface through the adhesive layer to the dry paint layer.

The embodiment of FIGS. 6 and 7 show separate support (reinforcing) and barrier layers. In addition, the barrier layer 60 may be included as a layer in the FIG. 6 embodiment. In this instance, the barrier layer may be applied between the dry paint layer and the support (reinforcing) layer, or the barrier layer may be applied between the adhesive layer and the support layer.

The dry paint layer 22 may have a thickness generally of about 0.5 to about 1.5 mils, in one embodiment about 0.5 to about 1.2 mils, and in another embodiment from about 0.5 to about 0.9 mil. The thickness of the adhesive layer may range generally from about 0.4 to about one mil, in one embodiment from about 0.4 to about 0.8 mil, and in another embodiment from about 0.4 to about 0.6 mil. The thickness of the release liner may range generally from about 0.5 to about 2 mils, in one embodiment from about 0.5 to about 1.5 mils, and in another embodiment from about 0.85 to about 1.05 mils. The thickness of the matte release coat layer may range generally from about 0.05 to about 0.3 mil, and in one embodiment from about 0.1 to about 0.2 mil. The thickness of the adhesive release coat layer may range from about 0.04 to about 0.2 mil, in one embodiment from about 0.04 to about 0.15 mil, and in another embodiment from about 0.04 to about 0.08 mil. The thickness of the outer clear coat layer may range generally from about 0.05 to from about 0.4 mil, and in one embodiment from about 0.05 to about 0.3 mil.

The thickness of the decorative print coat layers may range from about 0.02 to about 0.15 mil, and in one embodiment from about 0.02 to about 0.08 mils.

The reinforcing layer may have a thickness generally of about 0.3 to about 1.4 mils. In one embodiment the thickness can be about 0.3 to about 1.1 mils, in another embodiment about 0.3 to about 0.8 mil, and in a further embodiment about 0.3 to about 0.5 mil. When the reinforcing layer is used, the overall thickness of the combination of the dry paint layer and the support layer may be in the range of about 0.5 to about 1.5 mils, in another embodiment about 0.5 to about 1.2 mils, and in a further embodiment from about 0.5 to about 0.9 mil.

The barrier layer may have a thickness in the range of about 0.01 to about 0.1 mil, and in one embodiment about 0.05 to about 0.1 mil, and in another embodiment from about 0.01 to about 0.02 mil.

Each of the foregoing thicknesses are dry film thicknesses. The laminates may have any width or length that is suitable for its end use. For example, the width may range from about one to about 200 cm, and in one embodiment from 10 to 100 cm, and in another embodiment from about 30 to about 40 cm. The length may range from about 10 to about 6500 meters, and in one embodiment from about 15 to about 1000 meters. The laminates may take the form of flat sheets or as a self-wound roll form as illustrated in FIG. 2.

Dry Paint Layer

The dry paint layers may comprise independently one or more polymeric binders or resins, and one or more pigments. The reinforcing layer and barrier layer may comprise one or more polymeric binders or resins, and optionally one or more pigments. The transparent outer clear coat layer may comprise one or more polymeric binders or resins. These layers may be made from solvent cast liquid coating or paint compositions

comprising the one or more binders or resins and one or more pigments (if used). These compositions may be dispersed in water or one or more organic solvents, and optionally may contain one or more additional additives for controlling properties such as rheological properties or barrier properties. The dry paint layers, or the transparent outer clear coat layer, or the reinforcing layer or barrier layer may each comprise independently one or more extruded layers.

The binder or resin may comprise any binder or resin conventionally used in coating or paint formulations. The binder may comprise a thermoplastic or thermosetting resin. The binder or resin may be a synthetic resin or a natural resin. The binder or resin may comprise a film forming material which may be cast as a solvent-based coating or in one embodiment may be an extrudable film forming material. Examples of useful binders or resins generally include acrylic, vinyl, polyester, alkyd, butadiene, styrene, urethane and epoxy resins and phthalic acid or anhydride resins, and mixtures thereof. More specifically, the binder or resin may include one or more polystyrenes, polyolefins, polyamides, polyesters, polycarbonates, polyvinyl chloride, polyvinyl alcohol, polyethylene vinyl alcohol, polyurethanes, polyacrylates, polyvinyl acetates, ionomer resins, and mixtures thereof.

The binder or resin may comprise vinyl and vinylidene polymers or copolymers containing units such as vinyl acetate, vinyl chloride, and vinylidene chloride; hydrocarbon polymers and copolymers containing ethylene or propylene units and oxygenated or halogenated derivatives of ether, butadiene, oxygenated butadiene, isoprene, oxygenated isoprene, butadiene-styrene, butadiene vinyl toluene, and isoprene-styrene; polymers or copolymers containing units of

acrylic acid, methacrylic acid, their esters, or acrylonitrile; vinylic hydrocarbon monomers reacted with unsaturated materials such as the reaction product of maleic acid or anhydride with styrene; and, broadly, various other resinous rubber-like elastomeric latex polymers and copolymers of ethylenically unsaturated monomers and polymers obtainable in stable aqueous latex form. The binder or resin may comprise a copolymer of vinyl chloride and vinyl acetate.

The polyolefins may be characterized as having a melt index or melt flow rate of less than about 30, and in one embodiment less than about 20, and in one embodiment less than about 10 as determined by ASTM Test Method 1238. The polyolefins include polymers and copolymers of ethylene, propylene, 1-butene, etc., or blends of mixtures of such polymers and copolymers.

Various polyethylenes may be used including low, medium, and high density polyethylenes. The low density range for the polyethylenes may be from about 0.910 to about 0.925 g/cm³, the medium density range may be from about 0.925 to about 0.940 g/cm³, and the high density range may be from about 0.940 to about 0.965 g/cm³. An example of a useful low density polyethylene is Rexene 1017 available from Huntsman.

The propylene homopolymers which may be used either alone or in combination with a propylene copolymer include a variety of propylene homopolymers such as those having melt flow rates from about 0.5 to about 20 as determined by ASTM Test D 1238, condition L.

The polyamide resins include resins available from EMS American Grilon Inc., Sumter, SC. under the general tradename Grivory such as CF-65, CR-9, XE-3303 and G-21. The polyamide resins also include those available from, for example, Union Carbide of Wayne, New Jersey under the Uni-Rez product line, and

dimer-based polyamide resins available from Bostik, Emery, Fuller, and Henkel (under the Versamid product line).

The polystyrenes include homopolymers as well as copolymers of styrene and substituted styrene such as alpha-methyl styrene. Examples of styrene copolymers and terpolymers include: acrylonitrile-butene-styrene (ABS); styrene-acrylonitrile copolymers (SAN); styrene butadiene (SB); styrene-maleic anhydride (SMA); and styrene-methyl methacrylate (SMMA); etc.

The polyurethanes include aliphatic as well as aromatic polyurethanes.

The polyesters may be prepared from various glycols or polyols and one or more aliphatic or aromatic carboxylic acids. Polyethylene terephthalate (PET) and PETG (PET modified with cyclohexanedimethanol) are useful film forming materials which are available from a variety of commercial sources including Eastman. For example, Kodar 6763 is a PETG available from Eastman Chemical. Another useful polyester from DuPont is Sellar PT-8307 which is polyethylene terephthalate.

Acrylate polymers and copolymers and alkylene vinyl acetate resins (e.g., EVA polymers) may be used. Examples include Escorene UL-7520 (Exxon), a copolymer of ethylene with 19.3% vinyl acetate; Nucrell 699 (DuPont), an ethylene copolymer containing 11% of methacrylic acid, etc.

Ionomer resins (polyolefins containing ionic bonding of molecular chains) may be used. Examples of ionomers include ionomeric ethylene copolymers such as Surlyn 1706 (DuPont) and Surlyn 1702 from DuPont.

Polycarbonates also are useful, and these are available from the Dow Chemical Co. (Calibre) G.E. Plastics (Lexan) and Bayer (Makrolon).

The pigment may be any pigment used in making decorative coatings. These include opacifying pigments, such as titanium dioxide and zinc oxide, as well as tinting pigments such as carbon black, yellow oxides, brown oxides, tan oxides, raw and burnt sienna or umber, chromium oxide green, phthalocyanine green, phthalocyanine blue, ultramarine blue, cadmium pigments, and chromium pigments. The pigments include organic reds such as azo reds, quinacridone red and perylene red as well as organic yellows such as diarylide yellow. Mixed metal oxide pigments may be used. Filler pigments such as clay, silica, talc, mica, woloastonite wood flour, barium sulfate, calcium carbonate, aluminum silicate, and the like can be added as well in conventional amounts traditionally used in coating and paint formulations.

The solvent may be an organic-based solvent, such as a ketone, ester, aliphatic compound, aromatic compound, alcohol, glycol, glycol ether, etc. These include methylethyl ketone, methylisobutyl ketone, ethyl acetate, white spirits, alkanes, cycloalkanes, benzene, hydrocarbon substituted aromatic compounds (e.g., toluene, the xylenes, etc.), isoparaffinic solvents, and combinations of two or more thereof. Alternatively, water or a water-based solution may be used to form an aqueous emulsion with the binder or resin. Water-based solutions include water-alcohol mixtures. The solvent or water is sufficiently volatile so that when applied to a substrate, the solvent evaporates leaving behind the binder or resin, pigment (if used), and any other additional non-volatile components.

Additional ingredients that may be used include wetting agents; plasticizers; suspension aids; thixotropic agents such as silica; water repellant additives such as polysiloxane

compounds; fire retardant additives; biocides; defoamers; and flow agents.

The pigment concentration for the liquid paint or coating composition used to form the dry paint layers may range from about 10 to about 30% by weight, and in one embodiment about 13 to about 27% by weight. The binder or resin concentration may range from about 20 to about 40% by weight, and in one embodiment about 22 to about 37% by weight. The water or organic solvent concentration may range from about 30 to about 70% by weight, and in one embodiment about 40 to about 60% by weight. The additional ingredients such as wetting agents, suspension agents, etc., may have concentrations up to about 5% by weight. The coating or paint compositions used in making the dry paint layers may have a pigment to binder volume concentration in the range of about 5 to about 35%, and in one embodiment 10 to about 30%.

The liquid paint or coating compositions used for making the dry paint layers may be blended using known techniques. The dry paint layer may comprise a single coat or multiple coats of paint and is in the form of a continuous layer, while the printed decorative layers may independently be in the form of continuous or discontinuous layers. When multiple coats for the dry paint layer are used, each coat may have the same or a different formulation. The print coats may have the same color or a different color than the dry paint layer, or the print coats may have the same color, or they may have colors that are different from each other. The dry paint layer may be used to provide background color while the print layers may be used to provide a desired pattern or design.

(a) Transparent Top Coat Layer

The transparent outer clear coat layer may comprise a single coating layer or multiple coats, and may comprise any of the resinous materials described above. When multiple coats are used, each coat may have the same or a different formulation. As mentioned previously, the outer clear coat layer may be solvent cast (aqueous or organic solvent based) or the outer clear coat layer may be extruded. The outer clear coat layer, in one embodiment, provides enhanced scuff resistance, stain resistance and/or recoatability to the dry paint film layer or layers underlying it. Enhanced recoatability facilitates the subsequent application of another dry paint film layer or printed decorative layer over it, or the application of conventional paint or decorative dry paint films.

(b) Reinforcing or Support Layer

The reinforcing or support layer may be formed from any of the binder or resin materials described above. This layer may be formed from a solution or an emulsion and applied using any of the coating techniques described below. This layer also may be extruded. The reinforcing layer may contain one or more of the above-described pigments to enhance opacity of the finished laminate. The concentration of pigment in the reinforcing layer, when used, may range up to about 10% by weight, and in one embodiment about 6 to about 10% by weight.

The dry paint layers, outer clear coat layer or reinforcing layer independently may contain inorganic fillers or other organic or inorganic additives to provide desired properties such as appearance properties (clear, opaque or colored films), durability and processing characteristics. Examples of useful materials include calcium carbonate,

titanium dioxide, metal particles, fibers, flame retardants, antioxidant compounds, heat stabilizers, light stabilizers, ultraviolet light stabilizers, antiblocking agents, processing aids, and acid acceptors.

One or more of the dry paint layers, outer clear coat layer or reinforcing layer may contain a minor amount of an adhesive resin to enhance the adhesion of the dry paint layer to the outer clear coat layer and/or the support layer. Also, or alternatively, tie coat layers of an adhesive resin can be used between the dry paint layers and either the outer clear coat layer or the reinforcing layer. The adhesive resin for the tie coat can be an acrylic resin adhesive, or it can be an ethylene/vinyl acetate copolymer adhesive such as those available from DuPont under the tradename Elvax. The adhesive resins available from DuPont under the tradename Bynel also may be used.

In one embodiment, the dry paint layers, the outer clear coat layer and/or the reinforcing layer are flexible, but non-stretchable and non-elastic at room temperature.

Adhesive Layer

The dry adhesive layer may comprise a pressure-sensitive adhesive (PSA) which bonds the decorative laminate to a substrate surface, under applied pressure, at room temperature. The adhesive layer may be a continuous or discontinuous layer, and it may comprise one or a mixture of two or more adhesives. The adhesive layer may be a patterned adhesive layer with relatively strong adhesive tack level in some areas and a relatively weak adhesive in other areas.

In one embodiment, the adhesive layer is a repositionable adhesive, having a low initial tack that allows slight movement of the laminate to allow positioning adjustments

prior to forming a permanent bond. In one embodiment, the adhesive has a suppressed initial level of tack at room temperature that allows the laminate to adhere to a substrate surface and be repositioned thereon followed by removal of the matte release liner from the decorative dry paint layer. The adhesive layer undergoes a subsequent buildup of adhesion due to the passage of time sufficient to permanently bond the dry paint layer to the substrate. In one embodiment, the adhesive layer is characterized by producing only a limited amount of ooze beyond the borders of the laminate when the laminate is applied to a substrate. In one embodiment, no ooze is produced.

15 In one embodiment of the invention described below, the pressure-sensitive adhesive comprises a cross-linked acrylic resinous material, and more particularly, a cross-linked acrylic emulsion. A particularly useful adhesive material comprises an internally cross-linked acrylic emulsion. These pressure-sensitive adhesive materials provide a useful combination of low tack, peel and flow properties with a sufficient level of cohesive strength at a useful (thin) coat weight for providing the differential release properties described below. High molecular weight acrylic adhesives and externally cross-linked acrylic adhesives also may be used to produce the desired combination of functional properties.

20 The adhesive may comprise a rubber based adhesive, acrylic adhesive, vinyl ether adhesive, silicone adhesive, or mixture of two or more thereof. The adhesive may be applied to the laminate as a hot melt, solvent-based or water based adhesive. The adhesive materials that are useful may contain as a major constituent an adhesive polymer such as an acrylic-type polymer; block copolymer; natural, reclaimed, or styrene-butadiene rubber; tackified natural or synthetic rubber; a

copolymer of ethylene and vinyl acetate; an ethylene-vinyl-acrylic terpolymer; polyisobutylene; or poly (vinyl ether). Other materials may be included in the adhesive such as tackifying resins, plasticizers, antioxidants, fillers, and waxes.

A description of useful pressure-sensitive adhesives may be found in *Encyclopedia of Polymer Science and Engineering*, Vol. 13. Wiley-Interscience Publishers (New York, 1988). Additional description of useful pressure-sensitive adhesives may be found in *Encyclopedia of Polymer Science and Technology*, Vol. 1, Interscience Publishers (New York, 1964).

Pressure-sensitive adhesives that may be used include the hot melt pressure-sensitive adhesives available from H.B. Fuller Company, St. Paul, Minn. as HM-1597, HL-2207-X, HL-2115-X, HL-2193-X. Other useful pressure-sensitive adhesives include those available from Century Adhesives Corporation, Columbus, Ohio.

Conventional PSAs, including silicone-based PSAs, rubber-based PSAs, and acrylic-based PSAs are useful. Another commercial example of a hot melt adhesive is H2187-01, sold by Ato Findley, Inc., of Wauwatosa, Wisconsin. In addition, rubber based block copolymer PSAs described in U.S. Patent 3,239,478 to Harlan also can be used. This patent is incorporated by reference for its disclosure of such hot melt adhesives.

The adhesive compositions may contain at least one solid tackifier resin component. A solid tackifier is defined herein as one having a softening point above 80°C. When the solid tackifier resin component is present, the adhesive compositions may comprise from about 40% to about 80% by weight of a thermoplastic elastomer component, in one embodiment from about 20% to about 60% by weight, and in

another embodiment from about 55% to about 65% by weight of a solid tackifier resin component. The solid tackifier reduces the modulus of the mixture sufficiently to build tack or adhesion. Also, solid tackifiers (particularly the higher molecular weight solid tackifiers (e.g., Mw greater than about 2000) and those having a lower dispersity (M_w/M_n = less than about 3) may be less sensitive to migration into the polymer film layer. This is desirable since migration of tackifier into the film layer may cause dimensional instability.

The solid tackifier resins include hydrocarbon resins, rosin, hydrogenated rosin, rosin esters, polyterpene resins, and other resins which exhibit the proper balance of properties. A variety of useful solid tackifier resins are available commercially such as terpene resins which are sold under the trademark Zonatac by Arizona Chemical Company, petroleum hydrocarbons resins such as the resins sold under the trademark Escorez by Exxon Chemical Company, or Wingtack 95, a synthetic tackifier resin available from Goodyear, Akron, Ohio.

The modulus of adhesive mixtures to be coextruded also may be lowered by the incorporation of liquid rubbers, i.e., liquid at room temperature. The liquid rubbers generally will have an Mw of at least 5,000 and more often at least 20,000. Incorporation of liquid rubbers in amounts of less than 10%, and even less than 5% by weight based on the overall weight of the adhesive formulation results in adhesives which are coextrudable with the polymeric film materials. The incorporation of a liquid rubber may produce an adhesive having increased tack and adhesion. Liquid block copolymers such as liquid styrene-isoprene block copolymers may be used. Other liquid rubbers which may be incorporated into the

adhesive mixture include liquid styrene-butadiene rubbers, liquid butadiene rubbers, ethylene-propylene rubbers, etc.

The adhesive layer also may contain one or more pigments to enhance the opacity of the paint film layers overlying it and permit use of thinner paint film layers to achieve desired levels of opacity. Any of the pigments identified above may be used. Examples include titanium dioxide and carbon black. The pigment volume concentration may range up to about 10%, in one embodiment from about 5% to about 10%, and in another embodiment from about 2% to about 8%.

The adhesive compositions also may include other materials such as antioxidants, heat and light stabilizers, ultraviolet light absorbers, fillers, colorants, antiblocking agents, reinforcing agents, and processing aids.

The adhesive compositions may contain inorganic fillers and other organic and inorganic additives to provide desired properties. Examples of useful fillers include calcium carbonate, titanium dioxide, metal particles, and fibers.

Barrier Layer

The barrier layer may comprise any of the acrylate polymers or copolymers described above, polyvinyl alcohol, copolymers derived from ethylene and vinyl acetate, and copolymers derived from ethylene, vinyl acetate and polyvinyl alcohol. The barrier layer may comprise a polymer blend derived from polyvinyl alcohol, urethane, Cymel 385 (a product of Cytec identified as a melamine formaldehyde resin) and a polyaziridine (e.g., NeoCryl CX100 which is identified as trimethol-tris N (methyl aziridinyl) proprionate and is available from Avecia Resins), the weight ration of polyvinyl alcohol to urethane in one embodiment being about 20:80. The

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following examples illustrate specific coating compositions
which may be used in forming the barrier layer:

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		<u>Percent by Weight</u>
	Barrier Layer No. 1	
	Elvacite 2042 (product of Ineos identified as an ethyl methacrylate copolymer)	20
10	Toluene	48
	Methyl ethyl ketone	32
	Barrier Layer No. 2	
15	Adcoat 61WG178 (product of Rohm and Haas identified as a solution of acrylic polymer)	55.55
	Syloid 234 (product of Grace Davidson identified as synthetic amorphous silica)	0.10
20	N-propanol	44.35
	Barrier Layer No. 3	
	Adcoat	74.07
25	N-propanol	25.83
	Syloid 234	0.10
	Barrier Layer No. 4	
	Adcoat 61WG178	55.55
30	N-propanol	44.35
	Syloid 234	0.10
	Desmodur CB 75N (product of Bayer identified as an oligomeric toluene diisocyanate)	0.44

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Barrier Layer No. 5

5	Adcoat 61WG178	74.07
	N-propanol	25.83
	Syloid 234	0.10
	Desmodur CB 75N	0.44

10 Barrier Layer No. 6

	Adcoat 61WG178	58.0
	R-900 TiO ₂ (product of DuPont identified as rutile titanium dioxide)	15.00
	N-propanol	24.0
15	Isobutanol	3.00

Barrier Layer No. 7

	Adcoat 61WG178	58.00
	R-900 TiO ₂	15.00
20	N-propanol	24.00
	Isobutanol	3.00
	Desmodur CB 75N	0.88

Barrier Layer No. 8

25	Air Vol 523 (product of Air Products identified as polyvinyl alcohol)	5.0
	Water	47.5
	Isopropanol	47.5

30 As mentioned previously, the substrate surface contacted
by the decorative laminate can comprise a painted surface
having pigment materials containing color constituents which
can migrate into the decorative film and through the adhesive
layer to the color layer, causing discoloration. The barrier

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layer stops or retards the transmission of undesired discoloration-causing pigments sufficient to maintain discoloration or color shift of the color layer to within a level which is essentially unnoticeable for a useful life of the decorative film. Normal use conditions under which the decorative film is applied and normally in use are defined as temperatures from about 4°C (40°F) to about 35°C (90°F), and more particularly, from about 15°C (60°F) to about 27°C (80°F). To approximate the amount of color shift that may occur during an estimated useful life of the film under normal use conditions, film samples are tested by accelerated aging techniques and measured for color shift under those conditions. (Higher temperatures accelerate migration of discoloration color constituents.) In one embodiment, color shift is measured by comparing the color of an interior latex test sample with an interior latex color standard and then subjecting the test sample to a 60°C (140°F) environment for approximately 400 hours (16 days). The test sample is then measured for color shift and compared with the standard to determine the amount of color shift. According to one test, color shift is measured under ASTM 805 test procedures, and the unit of measure is C.I.E. color units on the Δb^* (yellow/blue) scale, although other color shift measurements can be used to determine whether color shift is within a specified range. These color shift measuring techniques are useful in evaluating whether a color shift is acceptably low by measuring the color shift in a blue painted sample caused by migration of yellow color constituents from mono azo pigments or dyes. In one embodiment, the color shift is considered sufficiently low to be within an acceptable range if testing at 60°C for 400 hours produces a color shift equal to or less than about 0.30 C.I.E. Δb^* color units.

1 The barrier layer comprises a thin, flexible polymeric
film which, in one embodiment, can be cross-linked to enhance
5 barrier properties. One embodiment of the barrier layer
comprises a non-pigmented acrylic resinous material which is
cross-linked at a cross-linking density sufficient to retard
transmission of mono azo pigments to within the acceptable
level. One embodiment of this barrier layer comprises a
10 relatively low molecular weight acrylic polymer which is
cross-linked with a melamine resin. A low molecular weight
acrylic resin suitable for the barrier layer has a molecular
weight below about 100,000. One such cross-linked acrylic
barrier layer (identified in more detail in Example 9) is the
15 acrylic polymer (Adcoat 61WG178 from Rohm and Haas) which has
a molecular weight of about 50,000. The cross-linking
increases the molecular weight and raises the softening point
of the barrier coat and creates a network at the molecular
level that retards transmission of the azo color constituents
20 through the barrier layer.

 The use of a cross-linked polymeric material as a barrier
coat can be useful in producing the desired retardation, but
in some instances, the cross-linking of the resinous material
can reduce adhesion to the PSA layer. In some instances, it
25 is desirable to include a tie coat between the base coat and
the PSA layer. One tie coat layer which has been shown to
improve adhesion comprises a thin coating of a material
similar to the pigmented base coat layer used in the
decorative film. One example of such a tie coat is the
30 plasticized vinyl tie coat shown in Example 9.

 The PSA layer can be applied to the barrier coat by
direct coating or casting of the PSA onto the previously
formed barrier coat. Alternatively, the PSA can be separately
cast on a temporary carrier and then transfer-laminated from
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the carrier to the barrier coat. Experimental tests have shown that adhesion between the barrier coating and the adhesive and the resistance to migration of color constituents is better when the adhesive is coated directly onto the barrier coating as opposed to transfer-lamination of the cast adhesive.

In another embodiment, the barrier layer can be made from a thermoplastic (non-cross linked or lightly cross linked) polymeric material. One such material is the low molecular weight acrylic material (61WG178) described above. To increase the material's resistance to migration of color constituents, a fine particulate filler material or additive can be dispersed in the barrier material. The filler or additive can have scavenging properties, or properties similar to a laking agent to which migrating pigments can attach, or the filler material can physically retard transmission rate to a sufficiently low level. Materials that have been found to reduce, capture, or stop migration of mono azo pigments include fumed aluminum oxide, metal phosphate compounds and/or titanium dioxide, although other metal salts, or oxides, or metal compounds also can be used to produce similar results. One metal compound useful in the barrier coat comprises an aluminum zirconium phosphosilicate available as Xtain A from Halox. Tests have shown good color shift results for low molecular weight thermoplastic acrylic resinous barrier materials containing these types of filler or additive materials. These materials also reduce color shift in a cross-linked acrylic resinous barrier coat layer.

In one embodiment of the invention, in which the barrier coat comprises a thermoplastic resinous material containing a dispersed filler for retarding color transmission, adhesion to the PSA layer can be enhanced by addition of a dispersed

adhesion agent to the barrier coat. The low molecular weight thermoplastic acrylic barrier coat can have adhesion properties enhanced by addition of polyvinyl pyrrolidone homopolymer (PVP). This barrier coat produces good adhesion to PSA layers which are either direct-coated or transfer-laminated to the barrier coat. The PVP is compatible with the acrylic base polymer material and the solvents used in the system and also increases adhesion to the PSA layer. One source of the PVP is International Specialty Products (ISP) identified as PVP K80.

Another embodiment of the barrier layer comprises a thermoplastic polymeric material having a sufficiently high molecular weight to retard color transmission to within desirable limits. A suitable high molecular weight barrier material has a molecular weight in excess of 250,000. One barrier material comprises a high molecular weight acrylic resinous material such as a polymethyl methacrylate (PMMA) having a molecular weight of about 350,000. This barrier material can produce the acceptable color shift results without addition of adhesion promoters or additives and also can be used without an additional tie coat layer to promote adhesion to the PSA.

The barrier layer of this invention is applied at a sufficiently low coat weight to produce a dry film thickness within a range of about 0.05 to about 0.20 mil. The barrier coat is sufficiently thin so as to not add significant thickness to the decorative portion (excluding the release liner) of the multi-layer laminate. In one embodiment, film thickness of the barrier layer is not more than about ten percent (10%) of the total thickness of the decorative portion of the film.

The barrier layer also is resistant to softening at

elevated temperatures, and in one embodiment, the barrier layer has a glass transition temperature (T_g) greater than about 60°C.

The addition of the barrier layer and the adjoining tie coat layer (if used) does not impact the differential release properties of the decorative film. Adhesion of the barrier layer to the PSA layer is sufficient to not appreciably reduce the peel force characteristics of the laminate in its self-wound form as described herein.

Matte Release Liner

The release liner may independently comprise paper, polymer film, or a combination thereof. The release liner, in one embodiment, is thermally stable, non-elastomeric and non-stretchable at room temperature.

Although paper of any weight may be used as a release liner, paper having weights in the range of from about 30 to about 120 pounds per ream are useful, and papers having weights in the range of from about 60 to about 100 pounds per ream are preferred. The term "ream" as used herein equals 3000 square feet.

Alternatively, the release liner may independently comprise a polymeric film, and examples of polymeric films include polyolefin, polyester, and combinations thereof. The release liner preferably may be formed from a flexible, foldable, heat-resistant, substantially inelastic, self-supporting temporary carrier film or casting sheet as is known in the art of dry paint transfer films. The release liner is preferably an oriented polyester film such as polyethylene terephthalate (PET) available as Mylar, a trademark of DuPont, or Hoechst Celanese Hostaphan 2000 polyester film, for example.

5 The release liner provides structural integrity to the laminate until the liner is removed upon application of the laminate to a substrate surface.

10 The matte release coat layer may comprise any of the above identified binders or resins which provide a level of tack or adherence between the release coat layer and the decorative dry paint layer, which may comprise either the color coat layer, the outer clear coat layer, or the decorative print layer. The tack level of the matte release coat layer is sufficient to prevent separation of the release coat layer from the adhered dry paint layer during the process of forming the dry paint transfer laminate and during normal handling of the laminate, including forming it in its self-wound orientation, unwinding it, and applying it to the substrate surface. The matte release coat also continues to have sufficient release properties to facilitate separation between the release coat layer and the adhered dry paint layer after having applied the laminate to the substrate.

20 The matte release coat formulation comprises a coating which can be applied to the release liner by conventional casting techniques such as gravure printing. The preferred coating composition is a thermosetting resinous material which, when exposed to heat for drying it, also cross links and permanently bonds as a surface film adhered to the release liner. The solids contained in the matte release coat preferably include, as a principal component, one or more crosslinking agents to provide good adhesion of the dried crosslinked coating to a polyester carrier film. In one embodiment, the matte release coat formulation includes a primary crosslinking resin such as a melamine resin that controls crosslinking and produces adhesion to the polyester carrier film. A presently preferred crosslinking resin is

hexamethoxy methyl resin such as Cymel 303. A suitable primary functional resin is a vinyl resin such as a medium molecular weight vinyl chloride-vinyl acetate resin known as VAGH. The vinyl resin can be present in an amount up to about 20% of the total solids in the matte release coat. In addition, the matte release coat can include a secondary functional resin to improve release of the top surface of the decorative dry paint layer from the matte release coat. In one embodiment, the secondary functional resin can be an acrylic-modified alkyd resin such as the resin known as Chempol 13 1501 or Lankyd 13-1245. This secondary functional resin comprises from about one percent to about 16% of the total solids, by weight, of the matte release coat. The matte release coat further includes a suitable catalyst for accelerating the crosslinking process, typically comprising from about one percent to about eight percent of the total solids in the matte release coat, by weight.

The resinous components of the matte release coat composition are combined with suitable solvents. In one embodiment, the resins are mixed with a primary resin solvent such as methyl isobutyl ketone (MIBK) which comprises from about 65% to about 85% of the total solvent in the formulation. A secondary resin solvent, such as isopropyl alcohol (IPOH), is useful in retarding crosslinking of resins in solution. The secondary resin solvent preferably comprises from about 5% to about 20% of the total solvent.

The matte release coat formulation is prepared by dissolving the primary functional resin in the primary and secondary resin solvents by mixing and then adding the secondary functional resin together with a primary matting agent, preferably in the form of a filler comprising a fine particulate inert inorganic material. In one embodiment, the

filler comprises aluminum silicate with an average particle size of about 4.8 microns. In another embodiment, the filler can comprise talc. The filler contained in the formulation comprises up to about 50% of the total solids in the matte release coat. In one embodiment, the talc filler material comprises from about 40% to about 50% of the total solids contained in the matte release coat. The fine particulate filler is thoroughly dispersed in the resin and resin solvent blend, preferably under elevated temperatures from about 100°F to about 120°F.

In use, when the matte release layer dries and cross links, it forms a chemical matte coating on the surface of the carrier sheet. The matte surface is controlled by the amount and particle size of the filler. The fine particles project through the dried exterior surface of the matte release coat to form, on a microscopic scale, a surface with a microroughness that transfers a replicated microroughness to the exposed surface of the dried outer clear coat or dry paint layer. This produces light scattering, resulting in a flat or low surface gloss matte finish on the top surface of the decorative dry paint layer.

In one embodiment a matte release coat formulation useful for this invention contains no significant amount of a silicone-based release material and/or a wax-based component. Such materials may be useful in providing release properties at high temperatures; but the matte release coat of this invention, in one embodiment, comprises a formulation that, in the absence of a silicone-based release material or a wax-based component, provides a useful combination of room temperature release, adherence of the release liner to the dry paint layer, and transfer of the matte surface to the exposed surface of the dry paint layer. Stated another way, the matte

release coat has a hardened state at room temperature and is made from a resinous material that contains (1) a surfacing component that forms a matte release surface, (2) an adhesion component for releasably adhering the matte release surface to the dry paint layer, and (3) a release component that releases the matte release surface from contact with the dry paint layer at room temperature to transfer the matte surface finish from the matte release surface to the exposed surface of the dry paint layer.

In one embodiment, the matte release coat comprises, on a solids basis, from about 10% to about 30% by weight alkyd resin; from about 10% to about 30% by weight vinyl resin; from about 20% to about 35% by weight melamine crosslinking resin; and from about 5% to about 10% catalyst. The balance of the solids comprises the fine particulate filler, e.g. talc, as described previously.

In one embodiment, the weight ratio of particulates to resin or binder may range up to about 1.1:1, in one embodiment from about 0.7:1 to about 1.1:1, in another embodiment from about 0.7:1 to about 0.9:1, and in a further embodiment from about 0.9:1 to about 1.1:1.

The gloss transferred to the outer surface of the dry paint layer can be controlled by a combination of release coat formulations and the composition of the outer surface layer of dry paint in contact with the release coat. In one embodiment, an 85° gloss of less than about 10 gloss units can be transferred to dry paint films having a monocoat or base coat/clear coat finish comprised of urethane, acrylic and/or vinyl resinous paint layers. The preferred release coat comprises an acrylic/vinyl blend containing a micro-particle filler. In another embodiment, 85° gloss measurements of less than about 35 gloss units can be transferred to dry paint

films having a monocoat or base coat/clear coat finish comprised of urethane, acrylic and/or vinyl resinous paint layers. The preferred release coat comprises an acrylic modified alkyd resin and/or vinyl resins containing dispersed microparticles.

The carrier film or release liner is typically contained on a supply roll from which the carrier is unwound and passed to a gravure print station where the matte release coat is coated onto the release liner. The release liner containing the matte release coat is then passed through a drying oven operated at a temperature from about 325°F to about 350°F, sufficient for drying and crosslinking the matte release coat. In the first stage drying oven, the matte release coat is sufficiently cross-linked to permanently bond it to the carrier sheet. Preferably, the matte release coat is coated and dried to a coat weight (dry) from about 3 to about 6 gsm.

The adhesive release coat layer may comprise any release coating composition known in the art. Silicone release coating compositions may be used. The silicone release coating compositions typically comprise polyorganosiloxanes such as polydimethylsiloxanes. The silicone release coating composition used in this invention may be room temperature cured, thermally cured, or radiation cured. Generally, the room temperature and thermally curable compositions comprise at least one polyorganosiloxane and at least one catalyst (or curing agent) for such polyorganosiloxane(s). These compositions may also contain at least one cure accelerator and/or adhesivity promoter.

Each of the layers in the multi-layer laminate may be independently applied and dried and/or cured using known techniques. The application techniques include gravure, reverse gravure, offset gravure, roll coating, brushing,

knife-over roll, metering rod, reverse roll coating, doctor knife, dipping, die coating, slot die coating, spraying, curtain coating, slide coating, slide curtain coating, extrusion, co-extrusion, flexographic, letter press, rotary screen, and flat screen. In one embodiment, the pressure sensitive adhesive layer may be applied using transfer lamination. The decorative print layers may be applied using known printing techniques including gravure, flexographic, silk screen, and ink jet printing. The applied layers may be dried and/or cured by exposure to heat or to known forms of ionizing or actinic non-ionizing radiation. Drying or curing temperatures that may be used may range from about 115°C to about 160°C, and in one embodiment about 140°C to about 150°C. Useful types of radiation include ultraviolet light and electron beam. The equipment for generating these forms of thermal or radiation drying and/or curing are well known to those skilled in the art.

Various layers of the multi-layer laminate also can be formed by extrusion and co-extrusion techniques identified above and described in more detail in U.S. Application No. 457,826 identified above and incorporated herein by reference. The dry paint layer or the support layer may be coextruded with the adhesive layer using separate extruders as illustrated in FIG. 8 or a dual die extruder as illustrated in FIG. 9. Referring to FIG. 8, release liner 70 is uncoiled from a roll 72 and advanced past an extrusion die 74 where it is coated with an adhesive layer 76, and then past an extrusion die 78 where a reinforcing or support layer 79 is coated onto the adhesive layer 76. The resulting co-extrudate is collected on a take-up roll 80. Referring to FIG. 9, the release liner 70 is advanced past a dual extrusion die 82 which simultaneously coats the release liner 70 with a

coextruded adhesive layer 84 and support layer 86. The resulting co-extrudate is collected on a take-up roll 88.

The dry paint transfer laminate illustrated in FIG. 1 may be made by applying the adhesive release coat to the lower surface of the release liner using one of the foregoing application techniques and then curing the release coat. The coat weight for the adhesive release coat layer may be in the range from about 0.1 to about one gram per square meter (gsm), and in one embodiment from about 0.25 to about 0.35 gsm. The matte release coat layer is then applied to the upper surface of release liner using one of the above described application techniques (e.g., gravure) and then dried or cured. The coat weight for the matte release coat may be in the range from about 2.5 to about 6.5 gsm, and in one embodiment, from about 4.5 to about 5.5 gsm. The liquid paint or coating composition for forming the pigmented dry paint layer is then applied to the surface of the matte release coat layer using one of the above described application techniques (e.g., reverse roll or slot die) and then dried or cured. The coat weight for the pigmented dry paint layer may range from about 20 to about 60 gsm, and in one embodiment about 30 to about 40 gsm. One or more coats may be applied. The pressure-sensitive adhesive layer is then applied to the upper surface of dry paint layer using one of the above indicated application techniques (e.g., slot die) and then dried or cured. The pressure sensitive adhesive may be applied using coating techniques or transfer lamination. The coat weight for the pressure sensitive adhesive layer may range from about 10 to about 30 gsm, and in one embodiment about 11 to about 17 gsm. The dry paint transfer laminate 20 may then be wound into roll form as illustrated in FIG. 2.

The dry paint transfer laminate illustrated in FIG. 3 may be made using the same procedure as the laminate 20 of FIG. 1, except that the transparent outer clear coat layer is applied to the matte release coat layer and then dried or cured prior to application of the pigmented dry paint film layer. The dry paint layer is then applied to the surface of the clear coat layer. The clear coat layer may be applied using one of the foregoing application techniques (e.g., gravure). The coat weight for the clear coat layer may range from about one to about 5 gsm, and in one embodiment about 2.5 to about 3.5 gsm. One or more coats may be applied. The dry paint transfer laminate may then be wound into a roll as illustrated in FIG. 2.

The dry paint transfer laminate illustrated in FIG. 4 may be made using the same procedure used as the laminate 20, except that the liquid paint composition for forming the printed decorative layer is applied to the surface of the transparent film layer and then cured prior to application of the dry paint film layer. The dry paint film layer is then applied to the surface of the printed decorative layer. The printed decorative layer may be applied using any of the foregoing printing techniques (e.g., gravure, flexographic, silk screen, or ink jet). The coat weight for the printed decorative layer may range from about 0.3 to about 2 gsm, and in one embodiment about 0.3 to about 0.7 gsm. The dry paint transfer laminate may then be wound into a roll as illustrated in FIG. 2.

The dry paint transfer laminate illustrated in FIG. 5 may be made using the same procedure as the laminate of FIG. 4, except that the liquid paint composition for forming the second printed decorative layer is applied to the surface of the transparent film layer and then dried or cured prior to

the application of the first printed decorative layer. The second printed decorative layer may be applied using any of the foregoing printing techniques (e.g., gravure, flexographic, silk screen, ink jet). The coat weight for the second printed decorative layer may range from about 0.3 to about 2 gsm, and in one embodiment about 0.3 to about 0.7 gsm. The dry paint transfer laminate may then be wound into a roll as illustrated in FIG. 2.

The dry paint transfer laminate illustrated in FIG. 6 may be made using the same procedure used for making the laminate 20 illustrated in FIG. 1, except that the reinforcing layer is adhered to the dry paint layer. The reinforcing layer may be coextruded with the adhesive layer and then the dry paint film layer may be coated (e.g., gravure) onto the reinforcing layer. The dry paint transfer laminate may then be wound into a roll as illustrated in FIG. 2.

The dry paint transfer laminate illustrated in FIG. 7 may be made using the same procedure used for making the laminate 20 illustrated in FIG. 1, except that the barrier layer is coated on the dry paint transfer layer. The dry paint transfer laminate may then be wound into a roll as illustrated in FIG. 2.

The dry paint transfer laminate may be made in a single production line or in multiple production lines or multiple production facilities. With multiple production lines or facilities, part of the laminate may be produced as a roll laminate, dried or cured, rolled up, transferred to the next production line or facility, unrolled, and further treated with the application of additional layers. For example, the dry paint layer and the adhesive layer may be formed in multiple lines, or they may be formed in sequence in a single

production line, or they may be simultaneously formed such as by coextrusion or multi-die coating methods.

The dry paint transfer laminate 20 may be used by unrolling the laminate from the roll illustrated in FIG. 2, and simultaneously applying the laminate to the substrate surface to be covered. The substrate may comprise any flat surface. The flat surface may comprise wall board, plastic sheet, metal sheet, composites, and the like. The substrate may comprise an interior (i.e., indoor) surface or an exterior (i.e., outdoor) surface. The laminate may be applied to a painted surface having various surface finishes, from flat, semi-gloss to glossy. The laminate is placed over the substrate with the adhesive layer in contact with the substrate. Pressure is applied, with repositioning if necessary, until the laminate is adhered to the surface. The release liner is then peeled off the front face of the decorative laminate, leaving the dry paint film layer adhered to the substrate by the adhesive layer. The dry paint transfer laminates shown in FIGS. 3 through 7 and in FIG. 10 also may be applied to a substrate surface in the same manner as the laminate 20.

Differential Release System

In one embodiment of the invention, the release properties of the laminate are controlled so that, in the embodiments illustrated in FIGS. 1-7 and FIG. 10, the release force required to separate the matte release coat layer from the dry paint layer (which may comprise the transparent layer, the color layer, or printed decorative layer) is greater than the release force required to separate the adhesive release coat layer from the pressure-sensitive adhesive layer.

In one embodiment, the carrier release force required to separate the matte release coat layer from the dry paint layer (i.e., the color layer, the clear coat layer, or the printed decorative layer) may be generally in the range from about 20 to about 180 grams per two inches (g/2 in), in one embodiment from 30 to about 150 g/2 in, and in another embodiment 40 to about 120 g/2 in. In other embodiments the release force range may be from 50 to about 100 g/2 in, from 50 to about 90 g/2 in, from about 70 to about 90 g/2 in, and from about 50 to about 65 g/2 in.

In one embodiment, the unwind release force required to separate the adhesive release coat layer from the pressure-sensitive adhesive layer is generally in the range from about 10 to about 150 g/2 in, in one embodiment from about 20 to about 150 g/2 in, in another embodiment about 20 to about 90 g/2 in, and in other embodiments from about 30 to about 150 g/2 in, about 30 to about 100 g/2 in, and about 30 to about 70 g/2 in.

The test method for determining these release forces involves measuring the force required to separate a two-inch wide release coated liner from the dry paint layer or from an adhesive coated substrate, with the release coated liner extending at an angle of 90° relative to the layer or substrate and being pulled at a rate of 300 inches per minute. The test is conducted at room temperature.

According to one embodiment of the invention, the decorative film contains a differential release system which enables the film to be unrolled from its self-wound form with the release liner maintaining continuous contact with the dry paint layer. As the decorative film is unrolled, the silicone-coated outer surface of the release liner preferentially releases from contact with the PSA side of the

film while the matte release coat side of the release liner maintains constant contact with the dry paint layer. This contact of the release liner with the dry paint layer is maintained throughout unwinding, application to the substrate surface, and any repositioning of the decorative film on the surface, until the release liner is ready to be peeled away from the decorative paint layer. The differential release system is adapted to maintain such preferential contact between the release liner and the dry paint layer because the dry paint layer is non-self-supporting, i.e., it has no structural integrity in and of itself, and therefore relies upon its contact with the release liner to provide the necessary structural support during unrolling, handling and repositioning, for example.

As mentioned previously, the release force between the release liner and the matte release layer (carrier release force) exceeds the release force between the silicone-coated side of the release liner and the PSA (unwind release force). Tests have shown that this "force differential" is dependent upon the rate or speed at which the materials at each interface are peeled away from each other. Inasmuch as the self-wound film, in use, may be unwound at different speeds, an objective of the differential release system is to ensure that the carrier release force exceeds the unwind release force over a wide range of release rates that are normally encountered during use. Generally speaking, this force differential is maintained over a wide range of speeds. During use, slow rates are encountered when unwinding a new roll or during the initial start of a roll on the surface. Medium to fast rates are encountered when the strip continues down the surface. In one embodiment, the force differential is maintained for a range of speeds up to about 300 inches per

minute for a 2 inch wide strip. In another embodiment, this force differential is maintained up to a speed of at least 600 inches per minute for a 2 inch wide strip.

The force needed to remove the PSA from the silicone side of the liner also should be less than the force needed to peel the carrier off the dry paint side in order to prevent peeling the carrier during slitting or unwinding, in addition to avoiding peeling of the carrier during unrolling, application to a surface, and repositioning on the surface. Unwind speeds in excess of 600 inches per minute may be encountered when cutting the film to individual roll sizes, but tests have shown that, in one embodiment, at such high speeds an undesired unwind response is not produced even when unwind release forces exceed carrier release force.

Such differential release forces can be measured, as described previously, by separating the liner from the matte release layer or the PSA layer in a two-inch wide strip at an angle of 90° pulled at a rate of 300 inches per minute with the tests conducted at room temperature. In one embodiment, the carrier release force is maintained higher than the unwind release force for release rates from about 6 inches per minute up to at least about 300 inches per minute. In another embodiment, the carrier release force is maintained within a range from about 45 to about 65 grams/2 inches over a wide range of release rates from about 6 inches per minute up to at least about 300 inches per minute. A corresponding unwind release force is maintained within a range from about 20 to about 40 grams/2 inches, over a range of liner release rates from about 12 to about 60 inches per minute.

Tests have shown that carrier release forces are maintained at a relatively uniform level across a wide range of release rates, whereas unwind release forces tend to

increase as release rates increase and can eventually exceed the carrier release forces above certain higher release rate levels. However, tests have shown that for release rates above about 300 inches per minute, an unwind release force in excess of the carrier release force does not negatively impact premature release of the release liner from the matte release layer during normal use conditions of the self-wound decorative film.

The composition of the PSA is coordinated with the composition of the dry paint layer in order to produce the desired differential release properties. The particular formulation used for the PSA can affect unwind release response. In addition, the composition of the dry paint layer which comes into contact with the matte release layer can affect release properties. In one embodiment, a relatively low unwind release force can be desirable if the carrier release force is relatively higher. However, there are limitations on the absolute magnitude of the carrier release force. Producing a substantially higher carrier release force compared to the lower unwind release force can maintain desired contact between the carrier and dry paint film during unwinding and application to a substrate surface; but if the carrier release force is too high, there may be difficulties in producing a proper release of the release liner from the dry paint layer after the PSA side of the laminate has been affixed to the substrate surface. If the carrier release force is too high, the user may experience difficulty in initially peeling the liner from the paint film; or removing the release liner may overcome the bond between the dry paint layer and the substrate and result in peeling the dry paint layer from the surface.

Therefore, another objective of the invention is to

produce a differential release system in which the carrier release force is higher than the unwind release force over a broad range of release rates, but the carrier release force level is maintained below a certain maximum force level. In one embodiment, a preferred dry paint layer comprises a transparent outer clear coat layer as described in Examples 7 and 9, in which the outer layer comprises a solvent-cast acrylic resinous material. This top coat material provides benefits of abrasion and stain resistance and repaintability in the finished film in addition to a useful carrier release force level when the matte release liner is peeled from the outer layer. The composition of the matte release coat in this embodiment comprises the alkyd/vinyl/melamine resinous composition of Examples 7 or 9, and the composition of the PSA comprises the adhesive formulation of Examples 7 or 9. In this embodiment, the carrier release force when peeled from the acrylic-based paint layer is maintained within a range of about 45 to about 65 grams per 2 inches. Corresponding unwind release force is maintained within a range of about 20 to about 40 grams per 2 inches, over a range of liner release rates from about 12 to at least about 60 inches per minute. It has been observed that the lower carrier release force level associated with the acrylic-based outer clear coat layer, i.e., below about 65 grams per 2 inches, provides sufficiently low carrier release properties to enable users to easily remove the release liner over a wide range of use conditions and carrier release rates.

By lowering the unwind release force response, the carrier release force then can be lowered to a more desirable level as mentioned previously. The PSA used in the present invention is preferably an internally cross-linked pressure-sensitive adhesive which lowers peel and tack levels. In one

embodiment, the internally cross-linked acrylate-based copolymer emulsion PSA of Example 9, for instance, produces unwind release levels that are sufficiently low to allow use of matte release coatings that produce carrier release responses at the more desirable lower levels as described previously. Use of a non-crosslinked (or lightly crosslinked) pressure-sensitive adhesive, which is softer, can have undesirable edge ooze characteristics during use; but in addition, it can produce higher peel and tack levels that undesirably increase the unwind release force in a direction toward the carrier release force.

The matte release coat composition also can control the carrier release force level. In the matte release coat formulation of Examples 7 and 9, the melamine crosslinking agent can be used to control the carrier release force level. The content of the alkyd resin and the lower molecular weight vinyl resin also can be controlled to lower release force. A useful combination of these components can produce desired room temperature adhesion to the release liner and release force response when peeling the release liner from the dry paint layer surface. The release coat composition also controls uniformity of and gloss level of the transferred matte surface.

As mentioned, the tack or peel level of the PSA also is controlled with respect to the surface to which the laminate is affixed. That is, the PSA in its dry form must have a low unwind release force from the silicone-coated release liner but also must have a sufficient level of tack to properly adhere to a substrate surface as well as providing sufficient repositionability.

A pressure sensitive adhesive useful for this invention is characterized by relatively low tack and peel force levels

and relatively low room temperature flow properties. Such adhesives, if they are too soft, can undesirably increase unwind force and can adversely affect repositioning of the paint film. Acrylic emulsion PSAs are particularly useful when such PSAs have a level of crosslinking that produces an adhesive material with a relatively high cohesive strength that yields a desirable combination of low tack, peel and flow properties. Examples of useful PSAs in which the level of crosslinking can be appropriately adjusted include acrylic emulsion PSAs such as pure polymer (butyl acrylate or 2-ethyl hexyl acrylate or 2-ethyl hexyl acrylate/butyl acrylate) PSAs or similar pigmented polymer and copolymer materials.

A particularly useful PSA for this invention is an internally cross-linked acrylic emulsion PSA such as a non-tackified cross-linked copolymer emulsion of butyl acrylate and 2-ethyl hexyl acrylate. This particular adhesive contains a crosslinking agent which controls the level of crosslinking and produces a desirable combination of low tack, peel and flow and relatively high cohesive strength at a useful low coat weight. This adhesive is available from Avery Dennison Corporation as product no. S-3506, or in its pigmented form as product no. S-3526.

Other multi-functional acrylic-based polymer and copolymer materials can be used to produce similar adhesive properties in their cross-linked form. In addition, other suitable pressure-sensitive adhesives for this invention can comprise high molecular weight acrylic emulsion adhesives. Such high molecular weight adhesives can behave in a manner similar to the cross-linked adhesives in producing low tack, peel and flow characteristics at sufficiently high cohesive strength. Exterior crosslinking agents also can be used to provide the desired level of crosslinking in such pressure

sensitive adhesives materials.

Another useful adhesive is a high molecular weight cross-linked acrylic emulsion adhesive (butyl acrylate/2-ethyl hexyl acrylate) available from Avery Dennison as product no. S-3000.

As mentioned previously, the PSA useful for this invention can be characterized, in part, as an adhesive that produces an unwind release force which is lower than the carrier release force, when releasing from contact with a silicone-coated release liner. The PSA also can be characterized, in part, by its level of adhesion to a substrate such as flat paint, glossy paint, primed drywall or stainless steel, for example. In one embodiment, the PSA formulation can be controlled to produce a low level of tack characterized by a looptack value within the range of about 0.8 to about 2.4 lbs/in, in which the adhesive is measured for adhesion to stainless steel and laminated to a 2 mil PET facestock, at a standard coat weight of 15 gsm.

In another embodiment, the PSA formulation can be controlled to produce a low level of 90° peel force adhesion, characterized by 15 minute peel adhesion to stainless steel in the range of 0.80 to 1.5 lbs/in for 2 mil PET; or 15 minute peel adhesion to flat painted surfaces of 0.05 to 0.30 lbs/in, or 15 minute peel adhesion to glossy painted surfaces of 0.20 to 0.40 lbs/in in which the adhesive is laminated to the dry paint transfer film with the release liner carrier.

In another embodiment, the PSA can be adjusted to produce a low peel force characterized by 90° peel adhesion values at 24 hours as follows: dry wall -- 0.30 to 0.50 lbs/in; flat paint -- 0.40 to 0.65 lbs/in; and glossy paint -- 0.60 to 0.90 lbs/in.

The PSA also can be characterized by its desired low flow properties at room temperature. Such characteristics can be

measured by its WPI (plasticity) value which in one embodiment has a WPI value from about 3.2 to about 3.8 mm.

The desired PSA also has a sufficient level of cohesive strength that enables the adhesive to permanently bond the paint film to the wall in the absence of a high level of tack. The level of crosslinking can effect such a cohesive strength, and in one embodiment, the cohesive strength is measured by a shear value of greater than 1,000 minutes (500 g 1/4 sq. in., 20 minute dwell, 14-16 gsm coat weight direct coated on 2 mil PET dried at 120°C for 5 minutes).

Examples 1 and 2

A polyethylene terephthalate (PET) release liner is coated on one side with a silicone release coating corresponding to the adhesive release coating layer. The thickness of the release coated liner is 0.92 mil, also known as Mitsubishi 92 gauge SLK.

A matte release coat is applied to the other side of the release liner using gravure at a coat weight of 6.5-7.75 gsm. The formulation for the matte release coat is as follows: 26 parts by weight methylisobutyl ketone, 6 parts by weight isopropanol, 34.8 parts by weight Lankyd 13-1425 (a product supplied by Akzo Resins identified as an acrylic modified alkyd), 2.6 parts by weight Elvacite 2042 (a product supplied by Lucite International identified as a polyethyl methacrylate polymer), 30 parts by weight Microtalc MP 15-38 (a product supplied by Barretts Minerals identified as a talc extender pigment), 2.5 parts by weight Cycat 4040 (a product supplied by Cytec identified as paratoluene sulfonic acid), and 8.7 parts by weight Cymel 303 (a product supplied by Cytec identified as a melamine resin). The matte release coat is dried using forced hot air at a temperature of 149°C which

crosslinks the resin and bonds the matte silicone coat to the polyester carrier. The talc particles project from the surface of the dried matte release coat to form a microroughened surface.

A transparent clear coat layer is applied to the matte release coat using gravure at a coat weight of 2.7-2.9 gsm and dried using forced hot air at a temperature of 120°C. The formulation for the clear coat layer is as follows: 46.7% by weight methyl ethyl ketone, 31.3% by weight toluene, 11% by weight VYNS (a product of Union Carbide identified as a vinyl chloride/vinyl acetate copolymer containing 5-20% by weight vinyl acetate), and 11% by weight Vitel 2200B (a product of Bostic identified as a polyester copolymer).

The following paint compositions are used to form a dry paint layer on the clear coat layer, one for Example 1 and the other for Example 2. The dry paint layer of Example 1 has a deep brown tone, while the dry paint layer of Example 2 has an orange pastel tone. In the following table, all numerical values are in parts by weight.

<u>Component</u>	<u>Example 1</u>	<u>Example 2</u>
Methylethyl ketone	66.7	66.7
Toluene	33.3	33.3
VYHH (product of Union Carbide identified as a vinyl chloride/vinyl acetate copolymer)	50.05	30.55
Edenol 9790 (a product of Cognis identified as a polyester		

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	plasticizer)	24.65	15.05
5	Yellow pigment 42 (iron oxide)	17.8	2.3
	Orange pigment 36 (monoazo benzimidazoline)	2.5	0.38
10	Black 7 (carbon black)	0.1	0.02
	White 6 (titanium dioxide)	4.9	51.7

15 The pigment-to-binder volume ratio for Example 1 is 10%,
and for Example 2 the ratio is 27%. The above paint
formulations are applied to the clear coat layer using a
reverse roll coater and are dried at a temperature of 135°C to
drive off the solvents. The dry film thickness of each of the
dry paint layers is 0.7 mil.

20 A pigmented pressure sensitive adhesive is then applied
to the dry paint layer at a coat weight of 14-20 gsm using
transfer lamination to provide an adhesive layer corresponding
to pressure sensitive adhesive layer 120. The adhesive is an
ethyl hexyl acrylate based PSA available from Avery Dennison
25 Corporation under product no. S-692N and the formulation for
the pressure sensitive adhesive is as follows: 70-90% by
weight 2-ethyl hexyl acrylate, 1-10% by weight acrylic acid,
10-20% by weight methyl acrylate, 3.7% UCD 1106E (a product of
Rohm and Haas identified as a titanium dioxide dispersion
30 concentrate), and 0.3% by weight of UCD 1507E (a product of
Rohm and Haas identified as a carbon black dispersion
concentrate).

35

Example 3

5 The procedure used for Examples 1 and 2 is repeated except that the following liquid paint composition is used to form the dry paint layer. In the following table, all numerical values are in parts by weight.

	<u>Component</u>	<u>Parts</u>
10	Methylethyl ketone	29.6
	Toluene	19.5
15	Vitel 2200 B	11.6
	Vitel 2650 (product of Bostic identified as a polyester copolymer)	11.5
20	R-900 (product of DuPont identified as titanium dioxide)	27.5
	955-39230 (product of Gibraltar Chemical Works identified as shading black)	0.2
25	99-34520 (product of Gibraltar Chemical Works identified as phthalo blue GS)	0.1
	955-37470 (product of Gibraltar Chemical Works identified as carbazole violet)	tint
30		

The foregoing paint composition has a light blue color. The dry film thickness of the dry paint film layer is 0.6-0.8 mil.

Example 4

A PET release liner is coated on one side with a silicone release coating corresponding to the adhesive release coat layer. The thickness of the release coated liner is 0.92 mil.

A matte release coat layer is applied to the other side of the release liner using gravure at a coat weight of 4.4-4.6 gsm. The formulation for the matte release coat is as follows: 50.54 parts by weight methylisobutyl ketone, 7.84 parts by weight isopropanol, 8.93 parts by weight Lankyd 13-1425, 10.68 parts by weight VAGH (product of Union Carbide identified as hydroxy modified polyvinyl chloride/polyvinyl acetate copolymer), 22 parts by weight Microtalc MP 15-38, 2 parts by weight Cycat 4040, and 6.8 parts by weight Cymel 303. The matte release coat is dried using forced hot air at a temperature of 149°C.

A first coat of a transparent outer clear coat layer is applied to the matte release coat using gravure at a coat weight of 1.3-2 gsm and dried using forced hot air at a temperature of 120°C. The dry film thickness is 0.05-0.1 mil. The formulation for this first clear coat layer is as follows: 41.5% by weight methyl ethyl ketone, 41.5% by weight methyl isobutyl ketone, and 17% by weight Elvacite 2042 (a product of Lucite International identified as a polymethyl methacrylate).

A second coat of a clear coat layer is applied over the first transparent layer using gravure at a coat weight of 1.0-1.5 gsm and dried using forced hot air at a temperature of 120°C. The dry film thickness is 0.03-0.1 mil. The formulation for this second transparent film layer coat is as follows: 41.5% by weight methyl ethyl ketone, 41.5% by weight methyl isobutyl ketone, and 17% by weight VYHH (a product of Union Carbide identified as a vinyl chloride/vinyl acetate copolymer containing 5-20% by weight vinyl acetate).

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 A decorative print layer is printed over the second
transparent clear coat layer at a coat weight of 3.0-3.2 gsm
5 and dried in hot air at a temperature of 120°C. The paint
composition for this decorative print layer has the following
formulation (all numerical values are in parts by weight):

	<u>Component</u>	<u>Parts</u>
10	Methylethyl ketone	42.6
	Methyl isobutyl ketone	38.7
15	VYHH	15.86
	DP 80110 (product of Gibraltar Chemical Works identified as containing methylethyl ketone, toluene, carbon black and acrylic polymer)	2.1
20		
	DP 36640 (product of Gibraltar Chemical Works identified as containing methyl ethyl ketone, toluene, quinacridone red, and acrylic polymer)	0.22
25		
	I8977 (product of Gibraltar Chemical Works identified as containing methyl ethyl ketone, toluene, R.S. Phthalo Blue, and acrylic polymer)	0.10
30		
	I8980 (product of Gibraltar Chemical Works identified as containing methyl ethyl ketone, toluene, isoindolinone	0.38
35		

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yellow and acrylic polymer)

5 An additional decorative print layer is printed over the
previous decorative print layer at a coat weight of 0.8 gsm
and dried in hot air at a temperature of 120°C. The paint
composition used for this decorative print layer has the
following formulation (all numerical values are in parts by
10 weight):

	<u>Component</u>	<u>Parts</u>
	Methylethyl ketone	42.85
15	Methyl isobutyl ketone	39.1
	VYHH	16.0
20	DP 80110	1.71
	DP 36640	0.18
	18977	0.18

25 The following paint composition is coated over the two
dried print coat layers at a coat weight of 30-32 gsm and
dried in hot air at a temperature of 120°C to provide a dry
paint. In the following table, all numerical values are in
30 parts by weight.

	<u>Component</u>	<u>Parts</u>
35	Methyl ethyl ketone	34

1	51256/WGM/A23	
	Toluene	16.7
5	VYHH	18.3
	Edenol 9790	9
10	AVI-0301-3 Orange (product of Gibraltar Chemical Works identified as containing methyl ethyl ketone, toluene, diarylide orange, VYHH and Edenol 9790)	8.9
15	AVI-0301-5 Magenta (product of Gibraltar Chemical Works identified as containing methyl ethyl ketone, toluene, Metal Azo Red, VYHH and Edenol 9790)	5.3
20	AVI-0301-6 Iron Red (product of Gibraltar Chemical Works identified as containing methyl ethyl ketone, toluene, Iron Oxide Red, VYHH and Edenol 9790)	3.7
25	AVI-0301-1 TiO ₂ White (product of Gibraltar Chemical Works identified as containing methyl ethyl ketone, toluene, titanium dioxide, VYHH and Edenol 9790)	3.52
30	AVI-0301-2 Carbon Black (product of Gibraltar Chemical Works identified as containing methyl ethyl ketone, toluene, carbon black, VYHH and Edenol 9790)	0.03

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5 A pigmented pressure sensitive adhesive is then applied
over the dry paint layer at a coat weight of 17 gsm using
transfer lamination to provide an adhesive layer corresponding
to pressure sensitive adhesive layer. The formulation for the
pressure sensitive adhesive is as follows: 96% by weight of a
non-tackified acrylic emulsion containing a cross-linked
copolymer of butyl acrylate and 2-ethyl hexyl acrylate, 3.7%
10 by weight UCD 1106E, and 0.3% by weight UCD 1507E.

Example 5

15 A PET release liner is coated on one side with a silicone
release coating. The thickness of the release coated liner is
0.92 mil.

20 A matte release coat is applied to the other side of the
release liner using gravure at a coat weight of 4.4-4.6 gsm.
The matte release coat is dried using forced hot air at a
temperature of 149°C. The formulation for the matte release
coat is as follows (all numerical values are in parts by
weight):

<u>Component</u>	<u>Parts</u>
25 Methyl isobutyl ketone	52.54
Elvacite 4402 (product of Lucite International identified as hydroxy ethyl methacrylate modified acrylic resin)	20.98
30 VYNS	1.35
Microtalc 15-38	22.85

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Byk 451 (product supplied by Byk 2.2
Chemie identified as blocked acid
catalyst)

Cymel 303	6.38
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A transparent clear coat layer is applied to the matte
10 release coat using a reverse roll coater at a coat weight of
13 gsm and dried using forced hot air at a temperature of
120°C. The dry film thickness is 0.4 mil. The formulation
for the transparent clear coat layer is as follows (all
numerical values are in parts by weight):

15

Component	Parts
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20	Rucothane CO-A-5002L (product of Ruco Chemical identified as polyester urethane)	62.5
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Toluene	18.75
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Isopropanol	18.75
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25

A decorative print layer is printed over the above indicated transparent film layer at a coat weight of 1 gsm and dried in hot air at a temperature of 120°C. The paint composition used for this decorative layer has the following formulation (all numerical values are in parts by weight):

30

Component	Parts
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Methyl ethyl ketone	25.67
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35

1	51256/WGM/A23	
	Methyl isobutyl ketone	22.0
5	VYHH	9.17
	I8980	3.5
10	DP 37251 (product of Gibraltar Chemical Works identified as containing perylene red, methyl ethyl ketone, toluene and acrylic polymer)	0.99
15	DP80110	1.0
20	DP39600 (product of Gibraltar Chemical Works identified as containing TiO ₂ , methyl ethyl ketone, toluene and acrylic polymer)	37.47
	I8977	0.20

25 The following paint composition is coated over the decorative print layer at a coat weight of 66 gsm and dried in hot air at a temperature of 138°C to form a dry paint layer. In the following table, all numerical values are in parts by weight:

30	<u>Component</u>	<u>Parts</u>
	Methyl isobutyl ketone	24.11
	Toluene	20.65

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VYHH	11.54
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5	R-900	38.4
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Acryloid B-72 (product of Rohm and Haas identified as an acrylic resin)	3.86
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10	I8980	2.6
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DP37251 0.21

DP80110 0.40

15

A pressure sensitive adhesive is then applied over the dry paint layer at a coat weight of 15-20 gsm using transfer lamination to provide an adhesive layer. The pressure sensitive adhesive is a non-tackified acrylic emulsion. The formulation for the pressure sensitive adhesive is as follows: 70-90% by weight 2-ethyl hexyl acrylate, 1-10% by weight acrylic acid, and 10-20% by weight methyl acrylate.

Example 6

25 A PET release liner is coated on one side with a silicone
release coating. The thickness of the release coated liner is
0.92 mil.

A matte release coat is applied to the other side of the release liner using gravure. The release coat is dried using forced hot air at a temperature of 148.9°C. The matte release coat is applied at a coat weight of 4.0-5.0 gsm. The formulation for the matte release coat is as follows (all numerical values are in parts by weight):

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	<u>Component</u>	<u>Parts</u>
5	Methyl isobutyl ketone	42.03
	Isopropanol	8.51
	Microtalc 15-38	23.87
10	Cymel 303	7.36
	Cycat 4040	1.8
15	VROH (product supplied by Union Carbide identified as a vinyl chloride/vinyl acetate copolymer with OH functionality)	16.43

20 A transparent clear coat layer is applied over the matte
release coat using a 2 mil byrd bar at a coat weight of 30 gsm
and dried using hot air at a temperature of 126.7°C. The
formulation for the transparent film layer is as follows (all
numerical values are in parts by weight):

25	<u>Component</u>	<u>Parts</u>
	Water	7.98
30	N-methyl pyrrolidone	4.79
	Texanol (product of Eastman Chemicals identified as an ester alcohol)	4.79

35

1

BYK 333 (product of Byk Chemie identified as a wetting agent)	0.4
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5

Vycar 351 (product of Noveon identified as a polyvinyl chloride copolymer emulsion)	79.81
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10	Antifoam PD-218 (product of Magrabar Chemical identified as an antifoam agent)	0.32
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	Rheolate 350 (product of Rheox, Inc.	1.92
15	identified as a thickener)	

The following paint composition is coated over the transparent clear coat film at a coat weight of 96 gsm and dried in hot air at a temperature of 126.7°C to form a dry paint film layer. In the following table, all numerical values are in parts by weight:

	<u>Component</u>	<u>Parts</u>
25	Water	18.28
	Surfynol CT-324 (product of Air Products identified as a surfactant)	0.98
30	R-900	32.88
	Vycar 460X45 (product of Noveon identified as a vinyl chloride/acrylic copolymer)	34.72

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Vycar 460X46 (product of Noveon identified 11.57
as a vinyl chloride/acrylic copolymer)

5 Antifoam PD-218 0.19

Byk 333 0.23

10 Rheolate 350 1.2

15 A pressure sensitive adhesive layer is then applied over
the dry paint layer at a coat weight of 17 gsm using transfer
lamination to provide an adhesive layer corresponding to
pressure sensitive adhesive layer. The formulation for the
pressure sensitive adhesive is as follows: 96% by weight of a
non-tackified emulsion containing a cross-linked copolymer of
butyl acrylate and 2-ethyl hexyl acrylate, 3.7% by weight UCD
1106E, and 0.3% by weight UCD 1507E.

20

Example 7

A PET release liner is coated on one side with a silicone
release coat layer. The thickness of the release coated liner
is 0.92 mil.

25 A matte release coat is applied to the other side of the
release liner using gravure at a coat weight of 4.4-4.6 gsm.
The formulation for the matte release coat is as follows:
50.54 parts by weight methyl isobutyl ketone, 7.84 parts by
weight isopropanol, 8.93 parts by weight Lankyd 13-1425, 10.68
30 parts by weight VAGH (product of Union Carbide identified as
hydroxy modified polyvinyl chloride/polyvinyl acetate
copolymer), 22 parts by weight Microtalc MP 15-38, 2 parts by
weight Cycat 4040, and 6.8 parts by weight Cymel 303. The

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matte release coat is dried using forced hot air at a temperature of 149°C.

A transparent clear coat layer is applied to the matte release coat using gravure at a coat weight of 12-16 gsm and dried using forced hot air at a temperature of 165°C. The dry film thickness is 0.35-0.5 mil. The formulation for this transparent film layer is as follows (all numerical values are in parts by weight):

<u>Component</u>	<u>Parts</u>
Cyclohexanone	69.3
Elvacite 2042	10.5
Solsperse 17000 (product of Avecia identified as a wetting agent)	0.1
Tinuvin 234 (product of Ciba identified as a light stabilizer)	0.6
Kynar 301F (product of Atofina identified as a polyvinyl fluoride homopolymer)	27.0
N-methyl-2-pyrrolidone	2.5

A decorative print layer is printed over the transparent coating layer at a coat weight of 0.3-1.2 gsm and dried in hot air at a temperature of 105°C. The paint composition used for this decorative layer has the following formulation (all numerical values are in parts by weight):

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	<u>Component</u>	<u>Parts</u>
5	Methylethyl ketone	36.0
	Methyl propyl ketone	35.1
10	Kynar 7201 (SL) (product of Atofina identified as a polyvinyl fluoride copolymer)	10.2
	Elvacite 2010 (product of Lucite International identified as a polymethyl methacrylate)	3.4
15	Tinuvin 234	0.27
	DP35740 (product of Gibraltar Chemical Works identified as a buff mixed metal oxide pigment concentrate)	0.10
20	DP35820 (product of Gibraltar Chemical Works identified as a brown mixed metal oxide pigment concentrate)	11.7
25	DP39040 (product of Gibraltar Chemical Works identified as a black mixed metal oxide pigment concentrate)	3.3
30	An additional decorative print layer is printed over the previous printed decorative layer at a coat weight of 0.3-1.2 gsm and dried in hot air at a temperature of 105°C. The paint composition used for this decorative print layer has the	

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following formulation (all numerical values are in parts by weight):

5

<u>Component</u>	<u>Parts</u>
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Methylethyl ketone	34.0
--------------------	------

10 Methyl propyl ketone	33.0
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Kynar 7201 (SL)	9.6
-----------------	-----

Elvacite 2010	3.2
---------------	-----

15

Tinuvin 234	0.25
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DP35740	14.4
---------	------

20 DP35820	5.0
--------------	-----

DP39040	3.2
---------	-----

25 The following paint composition is coated over the decorative print layers at a coat weight of 6-10 gsm and dried in hot air at a temperature of 105°C to provide a dry paint film layer corresponding to dry paint film layer 110. In the following table, all numerical values are in parts by weight.

<u>Component</u>	<u>Parts</u>
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Methyl ethyl ketone	27.6
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Methyl propyl ketone	26.3
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The formulation for the matte release coat is as follows:
50.54 parts by weight methylisobutyl ketone, 7.84 parts by
5 weight isopropanol, 8.93 parts by weight Lankyd 13-1425, 10.68
parts by weight VAGH (product of Union Carbide identified as
hydroxy modified polyvinyl chloride/polyvinyl acetate
copolymer), 22 parts by weight Microtalc MP 15-38, 2 parts by
weight Cycat 4040, and 6.8 parts by weight Cymel 303. The
10 matte release coat is dried using forced hot air at a
temperature of 149°C.

A decorative print layer is printed over the matte
release coat at a coat weight of 0.3-1.2 gsm and dried in hot
air at a temperature of 105°C. The paint composition used for
15 this decorative layer has the following formulation (all
numerical values are in parts by weight):

<u>Component</u>	<u>Parts</u>
20 Methylethyl ketone	36.0
Methyl propyl ketone	35.1
Kynar 7201 (SL) (product of Atofina 25 identified as a polyvinyl fluoride copolymer)	10.2
Elvacite 2010 (product of Lucite International identified as a polymethyl methacrylate)	3.4
30 Tinuvin 234	0.27
DP35740 (product of Gibraltar Chemical Works identified as a buff	0.10

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mixed metal oxide pigment concentrate)

5	DP35820 (product of Gibraltar Chemical Works identified as a brown mixed metal oxide pigment concentrate)	11.7
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	DP39040 (product of Gibraltar	3.3
10	Chemical Works identified as a black	
	mixed metal oxide pigment concentrate)	

15 An additional decorative print layer is printed over the previous printed decorative layer at a coat weight of 0.3-1.2 gsm and dried in hot air at a temperature of 105°C. The paint composition used for this decorative print layer has the following formulation (all numerical values are in parts by weight):

20	<u>Component</u>	<u>Parts</u>
	Methylethyl ketone	34.0
	Methyl propyl ketone	33.0
25	Kynar 7201 (SL)	9.6
	Elvacite 2010	3.2
30	Tinuvin 234	0.25
	DP35740	14.4
	DP35820	5.0
35		

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DP39040

3.2

5 The following paint composition is coated using
rotogravure over the decorative print layers at a coat weight
of 5-16 gsm and dried in hot air at a temperature of 105°C to
form a dry paint layer. In the following table, all numerical
values are in parts by weight.

10

<u>Component</u>	<u>Parts</u>
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Toluene	19.0
---------	------

15

Methyl ethyl ketone	23.6
---------------------	------

VYHH	5.8
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Edenol 9790	2.9
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20

DV39600 (product of Gibraltar	48.6
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Chemical identified as iron oxide red
pigment dispersion)

25

DV39420 (product of Gibraltar	0.07
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Chemical identified as carbon black
pigment dispersion)

DV36500 (product of Gibraltar	0.03
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30

Chemical identified as Pigment Red
178 pigment dispersion)

DV34130 (product of Gibraltar	0.10
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Chemical identified as Phtalo Blue RS

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1 **51256/WGM/A23**

pigment dispersion)

5 The following coating composition is coated over the dry paint layer using roll coating at a coat weight of 20-30 gsm and dried in hot air at a temperature of 105°C to form a support or reinforcing layer. In the following table, all numerical values are in parts by weight:

10

<u>Component</u>	<u>Parts</u>
Toluene	14.1
15 Methyl ethyl ketone	21.1
VYHH	13.2
Edenol 9790	6.6
20 DV39600	44.96
DV39420	0.04

25 A pigmented pressure sensitive adhesive is then applied over the coated layer corresponding to support layer 180 at a coat weight of 17 gsm using transfer lamination to provide an adhesive layer corresponding to pressure sensitive adhesive layer 120. The formulation for the pressure sensitive
30 adhesive is as follows: 96% by weight of a non-tackified acrylic emulsion containing a cross-linked copolymer of butyl acrylate and 2-ethyl hexyl acrylate, 3.7% by weight UCD 1106E, and 0.3% by weight UCD 1507E.

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Example 9

FIG. 10 illustrates one embodiment of the invention in which a decorative laminate 89 includes a dry paint layer coated in sequence onto a release liner 30 which includes a matte release coat 32 on one side and an adhesive release layer 34 on the side opposite the dry paint layer. The dry paint layer comprises an outer clear coat layer 44, one or more decorative print coats 48, and a color layer 22. A barrier layer 60 is bonded to the color layer and a tie coat 90 is bonded to the barrier coat and the PSA layer 28.

A PET liner is coated on one side with a silicone release coating corresponding to the adhesive release coat layer. The thickness of the silicone coated liner is 0.92 mil and comprises Mitsubishi 92 gauge SLK.

The matte release coat is applied to the other side of the release liner using gravure at a coat weight of 4.5 to 5.5 gsm. The formulation for the matte release coat is as follows (with all numerical values in parts by weight):

<u>Component</u>	<u>Parts</u>
Methyl isobutyl ketone (MiBK)	53.47
Isopropanol	6.49
Lankyd 13-1245 (product of Akzo Chemical, identified as an acrylic modified alkyd)	7.21
VAGH	8.72
EFKA 5055 (a carboxylic acid ester	1.10

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transparent top coat layer (with all numerical values in parts by weight) is as follows:

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<u>Component</u>	<u>Parts</u>
MEK	40
MiBK	41
10 Elvacite 2042	19

One or more decorative print coats having printing ink formulations similar to those described in previous examples are next printed over the transparent top coat layer following procedures as described previously.

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The following paint coat composition comprises a plasticized vinyl-based pigmented base coat having an epoxy stabilizer. The tie coat is coated over the decorative print layers, using roll coating at a coat weight of 33.0 to 36.0 gsm and dried in hot air at a temperature of 105°C to form a color coat layer. The dry film thickness is 0.65 to 0.73 mil. In the following table all numerical values are in parts by weight:

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<u>Component</u>	<u>Parts</u>
NiPar 820 (product of Angus Chemical identified as a blend of 80% nitro propane and 20% nitro ethane)	15.98
30 Xylene	23.95
Cyclohexanone	7.71

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	VYHH	12.76
5	Edenol 9790	6.38
	Stanclere T-883 (product of Adchross Chemical identified as a tin heat stabilizer)	0.06
10	EPON 828 (epoxy resin product of Shell)	0.26
	DV 39600 (Gibraltar TiO ₂ white pigment dispersion)	32.12
15	DV 396420 (Gibraltar carbon black pigment dispersion)	0.23
	DV 36500 (Gibraltar red pigment dispersion)	0.16
20	DV 34130 (Gibraltar phthalo blue pigment dispersion)	0.39

25 The following barrier coat layer is coated over the dried
color coat layer at a coat weight of 1.5 to 2.0 gsm. All
numerical values are in parts by weight:

	<u>Component</u>	<u>Parts</u>
30	Adcoat 61WG178 (a product of Rohm and Haas identified as acrylic polymer)	45
	Isopropanol	52

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barrier layer adheres to the color coat and the PSA adheres well to a similar color coat; so the tie coat is selected for its ability to provide good adhesion between the color coat and the PSA. The pigment component of the tie coat hardens the binder to a useful level.

The dry film thickness of the decorative laminate of this Example is within a preferred range of 1.30 to 1.60 mil. In the described example, the dry film thickness of the combined top coat, color coat, barrier coat, tie coat and PSA is from 1.35 to 1.51 mil.

A pigmented pressure sensitive adhesive layer is then applied to a carrier at a coat weight of 13 to 16 gsm. The dry film thickness of the PSA is from about 0.45 to 0.55 mil. The PSA is then applied to the tie coat by transfer lamination. The PSA is available from Avery Dennison Corporation under product no. S-3526 and the formulation for the PSA is as follows (with numerical values in parts by weight):

<u>Component</u>	<u>Parts</u>
S-3506 (product of Avery Dennison, Performance Polymers, identified as a cross-linked copolymer emulsion of butyl acrylate and 2-ethyl hexyl acrylate)	96.0
UCD 110GE (white TiO ₂ pigment dispersion from Rohm and Haas)	3.7
UCD 1507E (carbon black pigment dispersion from Rohm and Haas)	0.3

Examp1 10

5 Gloss measurements taken on the Byk-Mallinckrodt gloss
meter for various paint films as described herein produced the
following gloss readings:

10 (1) Release coat -- Elvacite 2899/VYNS at a ratio of
14.5:1, having a standard range of microtalc at 1.0 to 1.1:1
talc to polymer with Cymel 303

Top coat -- none

Color coat -- Rohm and Haas Acryloid B72/VYHH at a ratio
of 1:3

15 Gloss at 60° -- 3.4

Gloss at 85° -- 8.8

(2) Release coat -- Elvacite 2899/VYNS at a ratio of
14.5:1, having a standard range of microtalc at 1.0 to 1.1:1
talc to polymer with Cymel 303

20 Top coat -- Rucothane CO A 5002L urethane polymer

Color coat -- Rohm and Haas B72/VYHH at a ratio of 1:3

Gloss at 60° -- 4.9

Gloss at 85° -- 8.5

25 (3) Film having faux leather finish:

Release coat -- Acrylic modified alkyd with Cymel 303 and
standard range of microtalc at 1.0 to 1.1:1 talc to polymer.

Top coat -- Elvacite 2042 and VYHH/Vitel 220B at 1:1
ratio.

30 Gloss at 60° -- 2.2

Gloss at 85° -- 32.4

(4) Films having release coats and transparent top coat layers prepared according to Examples 7 and 9 produced gloss readings within a range from about 26 to about 30 at 85°.

Example 11

To measure the "force differential" in terms of carrier release force versus unwind release force, samples were produced in two-inch-wide by 12-inch long strips to simulate unwinding of a roll of the decorative film. A construction under test comprised the FIG. 3 embodiment having a transparent top coat, pigmented color layer, a PSA layer with the PSA side of the film exposed, and a release liner comprising a PET film having a matte release coat in contact with the top coat and an exposed silicone release coat on the opposite side of the release liner. In other tests, the construction was similar to that shown in FIG. 10 in which the same construction included the barrier layer and the tie coat layer.

One comparative test used test samples in which the compositions of the transparent top coat, the color coat and the PSA layer were generally as described in Examples 7 and 9, which included the Avery Dennison S-3506 PSA layer (an unpigmented form of Avery S-3526 adhesive). In other test samples, color coat and top coat formulations similar to Example 1 were used, in combination with the Avery S-3506 PSA layer. In further test samples, a construction involved the top coat and color coat formulations of Example 1 along with a different Avery Dennison PSA identified as S-692N adhesive.

The tests involved peeling the matte release layer away from the dry paint layer and peeling the silicone side of the release liner away from the PSA part of the sample. The tests were conducted at room temperature. In one test, separate

adhesive tapes were attached to the sides of the test samples to test the peel force at each interface with each tape extending in opposite directions, each at a 90° angle to the sample. The tests were performed on a movable sled having adjustable peel rates which, in one embodiment, were varied in increments from speeds as low as 12 inches per minute up to 1200 inches per minute. Peel forces were measured at progressive speed intervals and plotted on comparative force-versus-peel rate profiles.

The test results showed that carrier release force is reasonably uniform across a broad range of release rates, whereas unwind release forces tend to stay below the carrier release force at low speeds, but they approach and ultimately exceed the carrier force at higher speeds. Each profile generated by the tests was characterized by a cross-over release rate at which the unwind release force reaches and exceeds the carrier release force. Generally speaking, the self wound rolls that produced the best unwind response maintained a carrier release force in excess of the unwind release force at rates up to about 100 inches per minute. The test results showed that unwind force for the S-692N PSA approached carrier release force more rapidly than and exceeded it at a much lower propagation rate than the S-3506 PSA, which had superior unwind performance compared to the S-692N PSA. Such superior unwind performance was characterized by self-wound rolls of film containing the S-3506 adhesive being unwound without premature release of the release liner from the dry paint layer; whereas rolls of film containing the S-692N PSA experienced unreliable release response.

It was also observed that the S-3506 PSA exhibited lower tack levels and had less cold flow than the S-692N PSA. This was attributed to the S-3506 PSA having an internally cross-

linked structure which produced the lower tack levels and lower cold flow than the S-692N PSA which was not internally cross-linked and had higher tack levels, as well as higher cold flow. This difference in PSA properties caused the non-cross-linked PSA to stick more to the silicone side of the release liner and raised the unwind release force to levels that were too high and produced unreliable unwind response compared to the cross-linked PSA which produced more desirable (lower) unwind release force levels.

Example 12

Test panels containing barrier coats were prepared and tested for color shift. The test panels included a blue color layer similar to the color layer of Example 9 and a cross linked acrylic PSA layer, Avery's S-3506, similar to the PSA used in Example 9. The test films were applied to a yellow (Hansa Yellow 10G) painted surface and subjected to accelerated aging. The test films were measured for discoloration (color shift) caused by migration of azo-type color constituents that passed from the painted surface through the PSA layer to the color layer of the test sample. The test panels were prepared by using a dry paint color layer containing a plasticized vinyl-based paint layer containing a dispersed blue pigment. The S-3506 PSA was applied to the color layer. A medium yellow painted substrate was prepared using Behr 1300 deep base (5 ounces medium yellow per gallon base) applied at 7.5 mils wet coating to 3 mil polyester. The paint coat was allowed to dry for three hours minimum at room temperature then force air dried for five minutes at 250°F. The C.I.E. test procedures were used to measure Δb^* color change on the test panel at 60°C.

The following table shows six separate barrier coatings

which were evaluated for color shift using these test procedures. Test sample 1 was a cross-linked low molecular weight acrylic barrier coat; test samples 2 and 3 were thermoplastic low molecular weight acrylic barrier coats containing filler or additive materials for reducing color transmission; test samples 4 and 5 were thermoplastic low-molecular weight acrylic barrier layers that included the filler or additive materials, but also included PVP as an adhesion promoter; and test sample 6 was a high molecular weight thermoplastic acrylic barrier coat in the absence of any additive, filler or adhesion promoter. The materials contained in each test sample are shown in parts by weight.

Barrier Coat	Test Samples					
Materials	#1	#2	#3	#4	#5	#6
Adcoat 61WG178 acrylic	45.0	54.2	61.5	46.5	44.7	
Degussa Alum. Ox.		2.5	0.9	2.1	0.7	
Halox Xtain A		2.5	0.9	2.1	0.7	
IPOH	52.4	40.8	36.7	35.0	26.6	20.0
Cymel 303	2.4					
Cycat 4040	0.2					
PVP K80				14.3	27.3	
Toluene						70.7
Elvacite 2041 acrylic						9.3

The following test results for test samples #1 through #6 show color shift data for PSAs applied by both direct coating and by transfer-lamination.

Materials	Test Samples					
	#1	#2	#3	#4	#5	#6
Coat weight (gsm)	1.6	4.9	4.7	2.6	2.4	0.8
Direct adhesion	good	good	good	good	good	good
Color change 60°C (Δb^*)	0.38/ 1170 hrs		0.37/ 552 hrs		0.35/ 1002 hrs	0.4/ 1002 hrs
Transfer- lamination adhesion	poor	poor	poor	good	good	good
Color change 60°C (Δb^*)	0.47/ 162 hrs	0.97/ 239 hrs	0.61/ 330 hrs	0.89/ 201 hrs	0.39/ 376 hrs	0.38/ 552 hrs

A similar test was conducted using the cross-linked acrylic barrier coat of test sample #1 with the following tie coat (in parts by weight):

Tie Coat Material	Parts
MEK	25.22
MiBK	25.59
Dow VYHH	8.98
Plastolein 9790	4.49
Stanclere T-883	0.04
Dow EPON 828	0.18
DV39600 (Gibraltar White)	35.30
DV29420 (Gibraltar Black Disp.)	0.45
MiBK	4.00

The product having the tie coat was tested as 60°C for 401 hours. Samples for color shift measurement were taken throughout the roll. An average of 0.24 Δb^* color change resulted with a standard deviation of 0.06. The tie coating was used in this test because the adhesive was applied by transfer-lamination, and the tie coat was needed to increased adhesion between the barrier coat and the pressure sensitive adhesive.

Similar barrier polymer tests were conducted in which the C.I.E. Δb^* color shift was measured for different test samples, and then the color change that would occur at 60°C for 16 days was estimated.

Barrier Polymer	Coat wt. (gsm)	Final Hrs.	Proj. 16 days
(1) Thermoplastic acrylic - R & H 61WG178	2.5	400	1.82
(2) Same as (1)	2.5	308	4.86
(3) Cross-linked acrylic - R & H 61WG178/15 phr Cymel 303/1phr Cycat 4040	1.8	1337	0.25
(4) Same as (3)	1.6	497	0.37
(5) Same as (3)	1.6	227	0.96
(6) Cross-linked acrylic - R & H 61WG178/10 phr Cymel 303/1 phr Cycat 4040	1.8	1337	0.30
(7) Cross-linked acrylic- R & H 61WG178/15 phr Cymel 303/1 phr Cycat 4040/5 phr TiO ₂ /9 phr AlO _x	1.6	487	0.22
(8) Thermoplastic acrylic - R & H 61 WG 178/15 phr AlO _x /15 phr Xtain	2.0	427	0.12

General observations from these tests are that cross-linking of the low molecular weight acrylic barrier layer produces good color shift improvements into the acceptable range. Addition of titanium dioxide, aluminum oxide and similar metal compounds and oxides and salts further improve the barrier properties of both thermoplastic and cross-linked polymeric barrier layers.

The present invention has been described with respect to multilayer laminates used as a wall film for interior architectural applications, but the laminate also is useful in other applications as well. These would include exterior architectural applications such as siding panels and wall

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 surfaces; outdoor decorative items and signs; interior
automotive decorative and functional uses such as dashboards
5 and panels; and exterior automotive uses including automotive
body parts, trim parts and panels.

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